

MAR 1952

FDD  
FILE  
COPY

CLASSIFICATION C-O-N-F-I-D-E-N-T-I-A-L

CENTRAL INTELLIGENCE AGENCY

INFORMATION FROM

FOREIGN DOCUMENTS OR RADIO BROADCASTS

REPORT

CD NO.

50X1-HUM

COUNTRY USSR

SUBJECT Scientific-Chemistry - Hydrocarbons, peroxides,  
reaction kineticsDATE OF  
INFORMATION 1955HOW  
PUBLISHED Books, monthly periodicals, thrice-monthly  
periodical

DATE DIST. / Sept 1955

WHERE  
PUBLISHED Moscow, Leningrad, Kiev

NO. OF PAGES 13

DATE  
PUBLISHED 1952-1955

LANGUAGE Russian

SUPPLEMENT TO  
REPORT NO.

THIS DOCUMENT CONTAINS INFORMATION AFFECTING THE NATIONAL DEFENSE  
OF THE UNITED STATES, WITHIN THE MEANING OF TITLE 18, SECTIONS 793  
AND 794, OF THE U.S. CODE, AS AMENDED. ITS TRANSMISSION OR REVE-  
LATION OF ITS CONTENTS TO OR RECEIPT BY AN UNAUTHORIZED PERSON IS  
PROHIBITED BY LAW. THE REPRODUCTION OF THIS FORM IS PROHIBITED.

THIS IS UNEVALUATED INFORMATION

SOURCE As indicated.

USSR DEVELOPMENTS IN THE FIELD OF HYDROCARBON OXIDATION,  
CHEMICAL SYNTHESIS BASED ON PARTIAL OXIDATION  
OF HYDROCARBONS, AND KINETICS OF OXIDATION

[Comment: In recent USSR work on the subject of reaction kinetics, particularly as applied to the oxidation and other conversion of hydrocarbons, an increased emphasis on the utilization of hydrocarbons as a raw material for the chemical industry is discernible. One of the reasons for the trend towards petrochemical synthesis, which is apparent in recent USSR publications, may be an increased demand for liquid fuels of medium boiling range (kerosene for reaction motors and diesel fuel for tractors and trucks), combined with a correspondingly reduced demand for light fuels and aromatics, at least as far as aviation fuel is concerned (S. K. Makarov, D. I. Orochko, L. A. Potolovskiy, D. Kh. Teregulov, "The Petrochemical Trend in the Petroleum Conversion Industry," *Neftyanaya Promyshlennost'*, Vol 33, No 2, Moscow, February 1955, pages 67-71). If changes in the demand for automobile gasoline are disregarded, this shift from light fuels to fuels of medium boiling range makes an increased amount of light petroleum constituents available for conversion to petrochemical products and also reduces the losses due to cracking. The supply of light hydrocarbons available in the USSR for conversion to petrochemicals by direct oxidation, and by other processes, is augmented by the development and exploitation of natural gas fields. With the view of converting gaseous hydrocarbons to useful chemical products, homogenous catalytic reactions are being investigated and applied.

- 1 -

CLASSIFICATION C-O-N-F-I-D-E-N-T-I-A-L

STATE	NAVY	NSRD	DISTRIBUTION									
ARMY	AIR	FBI										

50X1-HUM

C-O-N-F-I-D-E-N-T-I-A-L

The practice of subjecting petroleum refining residues to thermal cracking, resulting in extensive dehydrogenation, and converting the dehydrogenated liquid products to motor fuels and other petroleum products by catalytic hydrogenation, is regarded as uneconomical by USSR petroleum chemists. According to S. R. Sergienko, thermo-catalytic conversion of petroleum residues, which leads to extensive destruction and is accompanied by the formation of coke, gas, and liquid products rich in aromatics and unsaturated hydrocarbons, cannot be regarded as a basic method for the conversion of distillation residues to motor fuels, but only as an intermediate step in which the crude material is prepared for further chemical conversion (S. R. Sergienko, "More About the Problem of Increasing the Degree of Utilization of Petroleum as a Crude Material," *Neftyanaya Promyshlennost'*, Vol 33, No 2, Moscow, February 1955, pages 71-8). S. K. Makarov et al, are also of the opinion that unless large quantities of butadiene, ethyl alcohol, fatty acids, detergents, and other chemicals are produced by petroleum combines in addition to fuels and lubricating oils, the cost of motor fuels and oils will become too high if the degree of conversion of crude petroleum is increased further, in conformity with the tendency that has been prevalent hitherto (S. K. Makarov, D. I. Orochko, L. A. Potolovskiy, D. Kh. Teregulov, "The Petrochemical Trend in the Petroleum Conversion Industry," *Neftyanaya Promyshlennost'*, Vol 33, No 2, Moscow, February 1955, pages 67-71).

Although there is a pronounced emphasis on supplying products needed by the consumer goods industry, and on using processes of the partial oxidation of hydrocarbons for the production of chemicals required for that purpose, the potential applications of the results of work in the general field of hydrocarbon oxidation in solving problems which have a bearing on the combustion of fuels, the detonation of explosive mixtures, and the production of some propellants are obvious from the outline given below. Methods for the isolation of peroxides to be used as additives to fuel, and in research on the oxidation of hydrocarbons with nitric acid, are of interest from this standpoint. The fact that there are frequent references to the use of pure oxygen rather than air in industrial oxidations is worthy of attention.

Although the work on inhibitors of the decomposition of hydrocarbons (see last section of this report) has no direct bearing on oxidation processes, it is of importance from the standpoint of the improving yields of unsaturated hydrocarbons obtained by oxidative cracking and improving the stability of hydrocarbons in general, whenever mixtures containing them are subjected to oxidative processes or other processes which may involve cracking. The work in question has been carried out at Saratov State University, i. e. in the vicinity of a major gas field. This suggests a primary interest of the investigators in the conversion of hydrocarbons found in natural gas. The fact that they have concentrated to some extent on investigating the stability and other properties of butadiene may be of importance in this connection.

Numbers in parentheses refer to appended sources.]

- 2 -

C-O-N-F-I-D-E-N-T-I-A-L

50X1-HUM

C-O-N-F-I-D-E-N-T-I-A-L

Work on Oxidation of Hydrocarbons

Work on the oxidation of hydrocarbons is being conducted on an extensive scale in the USSR. An All-Union conference on problems of the oxidation of hydrocarbons was held in Moscow 14-18 May 1951, by the Petroleum Institute, Academy of Sciences USSR. More than 30 reports dealing with various aspects of the oxidation of hydrocarbons were presented at the conference. The most important phases of work in this field, such as research on the mechanism of reactions of the oxidation of hydrocarbons and the results of industrial work based on the application of such reactions, were discussed. Furthermore, the results of work on the oxidation of hydrocarbons done in the USSR during the preceding 10 years were summarized. The most important problems of the theory and practical application of oxidation reactions were discussed in papers presented by N. N. Semenov, N. I. Chernozhukov, A. N. Bashkurov, K. I. Ivanov, I. P. Losev, Z. K. Mayzus and N. M. Emanuel', M. B. Neyman, V. Ya. Shtern, A. Yu. Rabinovich, V. K. Tsyskovskiy, and others. The principal papers presented at the conference were published in 1954 in a book entitled Problems of the Oxidation of Hydrocarbons. (1)

During recent years, the following significant results were achieved in USSR research on the oxidation of hydrocarbons:

1. N. N. Semenov's theory of the chain mechanism of reactions was found to explain, in a satisfactory manner, the reactions of hydrocarbon oxidation. Experimental investigations yielded extensive data which confirm that the most important processes of hydrocarbon oxidation proceed by a chain mechanism. The work in question made it possible to approach closer to a complete understanding of the processes of oxidation and combustion of hydrocarbon fuels in engines. (2,3).

2. Investigations conducted by S. S. Nametkin and A. N. Bashkurov and his collaborators clarified the mechanism of reactions leading to the formation of alcohols and carboxylic acids in the liquid-phase oxidation of saturated hydrocarbons by the oxygen of the air. Clarification of the dependence of the rate and direction of these reactions on temperature, the catalysts which are present, and other variables, made it possible to direct effectively the course of the process occurring in oxidations of this type. (2,4)

3. N. I. Chernozhukov and S. E. Kreyn, in their investigations on the oxidation of different types of hydrocarbons and hydrocarbon mixtures, established the relationships which govern the course of coupled oxidation reactions. The work in question is of great significance for the solution of practical problems connected with the production, storage, and use of motor fuels and lubricating oils. (2,5)

Conversion of Hydrocarbons to Peroxides

Research by K. I. Ivanov on the oxidation of hydrocarbons not only yielded new data which confirm that the oxidation of hydrocarbons proceeds by the peroxide mechanism, but also made it possible to develop original methods for the production, isolation, and storage of organic peroxides. (2,6,7) In Ivanov's work the peroxides were prepared by bubbling oxygen through liquid hydrocarbons in special equipment and subjecting the reaction mixture, consisting of oxygen and the hydrocarbon, to the action of ultraviolet light. New relationships pertaining to the mechanism of the oxidation of hydrocarbons to hydroperoxides were discovered by Ivanov and members of his group. In

- 3 -

C-O-N-F-I-D-E-N-T-I-A-L

C-O-N-F-I-D-E-N-T-I-A-L

50X1-HUM

addition to functioning as intermediate products in hydrocarbon oxidation, organic peroxides serve as initiators of the polymerization of unsaturated compounds in the production of synthetic rubber, as additives which lower the flash point of fuels in engines, as reagents, and as intermediate products in organic synthesis. (6,7)

Z. K. Mayzus and N. M. Emanuel' have carried out an investigation on the oxidation of hydrocarbons in the presence of hydrogen bromide. The aim of the work done by them was both a study of homogenous catalysis from the theoretical standpoint and an investigation of the kinetic relationships involved, with a view to applying reactions of this type on an industrial scale. In the course of this work it was demonstrated that hydroperoxides are formed as intermediate products which then decompose under the action of the hydrogen bromide, forming the final oxygenated product (e.g. acetone in the oxidation of propane). (8,16)

#### Industrial Synthesis Based on Oxidation of Hydrocarbons

The work of S. S. Nametkin, A. N. Bashkirov, K. I. Ivanov, S. S. Medvedev, G. S. Petrov, I. P. Losev, V. K. Tsyskovskiy, P. A. Moshkin, D. S. Velikovskiy, N. I. Chernozhukov, and other Soviet scientists has contributed to the introduction of a number of technological processes, based on the oxidation of hydrocarbons, into the petroleum and chemical industries. (2)

I. P. Losev and R. N. Smirnov have conducted investigations on the oxidation of petroleum hydrocarbons with nitric acid. Under the conditions studied by them, hydroxycarboxylic acids formed the principal product of the oxidation. (9)

According to V. K. Tsyskovskiy, either unsubstituted carboxylic acids or hydroxyacids are formed predominantly when kerosene, solar oil, or petrolatum is oxidized with air. The chemical composition of the products depends on the composition and concentration of the catalyst, the rate of oxidation, the temperature, the material from which the reaction equipment has been constructed, and other factors. By selecting the right conditions, products of the desired chemical composition can be obtained. While paraffin wax is a crude material which is best suited for the production of unsubstituted, straight-chain carboxylic acids, the prevailing impression that only acids which are similar to those found in animal and vegetable fats can be produced by the oxidation of petroleum hydrocarbons is erroneous.

The hydroxyacids (actually a mixture of hydroxyacids, ester acids, and esters of the estolide, lactide, and lactone series, referred to as "ester acids") proved to be a useful film-forming material for external protective coatings. They are at present being produced industrially in the USSR for this purpose. Oxidized petrolatum is used in the manufacture of special lubricants that comply with AT GOST 3823-47 [Autotractor State Standard 3823-47], of cooling liquids, and of other products. Carboxylic acids obtained by the oxidation of kerosene fractions have been found useful in the production of lubricating greases, rubber, solid and liquid detergents, plastics, paper, and other products. These acids are also effective flotation reagents and furthermore can be used to lower the surface hardness of metals. In 1947, a new type of solidol [hydrocarbon and carboxylic acids mixture for the production of lubricating grease] was introduced. This solidol (cf. GOST 4366-48) is manufactured by oxidizing paraffin wax. It proved to be in no way inferior to solidols containing natural fatty acids.

- 4 -

C-O-N-F-I-D-E-N-T-I-A-L

C-O-N-F-I-D-E-N-T-I-A-L

50X1-HUM

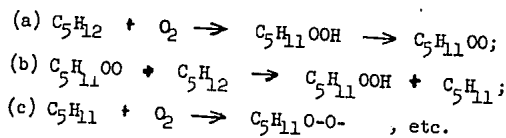
Work on producing the simplest carboxylic acids (those which are soluble in petroleum ether) by the oxidation of kerosene has also proved to be successful. (10)

### Cold-Flame Oxidation of Hydrocarbons and Its Industrial Applications

On the basis of N. N. Semenov's theory of chain reactions and A. N. Bakh's peroxide theory of hydrocarbon oxidation, which is now more generally accepted than W. Bone's hydroxyl theory and applies rigidly in homogeneous oxidations, USSR investigators have carried out a considerable amount of work on the oxidation of lower hydrocarbons ( $C_1-C_5$ ) to oxygen compounds, particularly with the view of producing alcohols. Research done by M. S. Furman and others indicated that the production of methyl alcohol and formaldehyde by the oxidation of methane or of natural gas is feasible if the reaction is carried out at a high pressure. Pressure favors the reaction, because oxidation of the hydrocarbons  $C_1-C_5$  (but not of hexane) proceeds in the gas phase. At atmospheric pressure, satisfactory yields of formaldehyde and methyl alcohol result only if the oxidation of methane is carried out in the presence of nitrogen oxides. The effect of homogeneous catalysts (of hydrogen bromide, based on work done by F. F. Rust and W. Vaughan in the US, and of chlorine, in research conducted by N. I. Zemlyanskiy, O. A. Prib, and M. Ya. Sharypkina) on the oxidation of methane has been investigated.

The cold-flame oxidation of lower hydrocarbons has been investigated by a number of Soviet scientists. The process in question consists in the oxidation of hydrocarbons with an inadequate quantity of oxygen at temperatures which are lower than those necessary for the combustion of the hydrocarbons. In this type of oxidation the formation of a considerable quantity of oxygen-containing compounds, particularly of aldehydes, takes place. M. B. Neyman and his coworkers established that in the cold-flame oxidation of methane the percentage of conversion of the hydrocarbon to the aldehyde may be as high as 50%. Cold-flame oxidation of propane yields an amount of oxidation products equal to 50% of the theoretical yield. These products contain 70% aldehydes. From the oxidation of propane at  $360^\circ$ , a certain quantity of methyl alcohol, ethyl alcohol, formic acid, and acetic acid was isolated. The cold-flame oxidation of light gasoline fractions, butenes, cracking gases, by-products of the manufacture of SK (synthetic rubber), etc. yielded reaction products which contained up to 25% aldehydes. However, the isolation of these aldehydes from the reaction mixture was complicated by the presence of a great number of oxygen-containing compounds. The reaction mixtures which result from this type of oxidation are sometimes so complex that the isolation and identification of individual compounds cannot be carried out.

Investigation of the mechanism of cold-flame oxidation of hydrocarbons and a study of the kinetics of this process led to the conclusion that the cold-flame oxidation of hydrocarbons is an autocatalytic process which is accelerated by the oxygen-containing substances that form during its course. This fact is confirmed by the existence of an induction period of oxidation, a period which is followed by a rapid oxidative reaction of the chain type. For example, the oxidation of pentane can be represented schematically as follows:

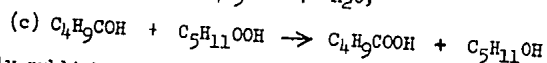
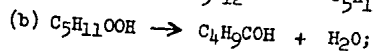
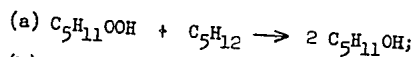


C-O-N-F-I-D-E-N-T-I-A-L

C-O-N-F-I-D-E-N-T-I-A-L

50X1-HUM

The hydroperoxides that form as intermediate products are either stabilized, so that they may be isolated from the final products, or decompose with the formation of alcohols, aldehydes, and acids, as shown in the following scheme:



A recently published paper by L. A. Repa and V. Ia. Shtern (*Doklady Akademii Nauk SSSR*, Vol 91, 1953, page 308) deals with the cold-flame oxidation of propane. In the course of an investigation of the kinetics of this oxidation, Repa and Shtern isolated a number of intermediate products, i.e. formaldehyde, acetaldehyde, peroxides, and various acids. They are of the opinion that both the cold-flame oxidation and the high-temperature oxidation of propane are based on the same chemical process. In view of the fact that cold-flame oxidation cannot be controlled with facility, this process has not yet been applied in industrial organic synthesis, as far as is known. (11)

The study of the so-called cold flames is of great importance in understanding the mechanism of the oxidation of hydrocarbons during the period preceding their combustion. The temperature of the cold flame produced by ethers, aldehydes, and hydrocarbons is considerably lower than the temperature of hot flames and usually exceeds that of the surrounding medium by only 50-200°.

In cold flames, considerable amounts of substances are formed which are merely unstable intermediate products, from the standpoint of the peroxide theory and also of the hydroxyl theory. As a result of investigations on the subject of cold flames carried out by foreign and USSR investigators (among the latter were R. S. Yakovlev, B. A. Ayvazov, and M. B. Neyman), the connection between the capacity of fuels to form a cold flame and their tendency to detonate in an internal combustion engine was noted.

This connection is easy to understand in the light of investigations which have established the dependence of the detonation wave of combustion on oxidation reactions and the formation of peroxides. Apparently, the reactions which take place prior to the formation of cold flames at low temperatures and pressures are similar to those taking place at high temperatures and pressures prior to the detonation in the engine. It follows, from work done by M. B. Neyman and his collaborators, that cold-flame oxidation of hydrocarbons with oxygen or air may be used in industrial organic synthesis for the large-scale production of aldehydes, acids, alcohols, and other compounds. The products of oxidation of the complex mixture of hydrocarbons of "motor fuel SK" in a cold flame were investigated by A. D. Petrov, Ye. B. Sokolova, and M. S. Fedotov. They identified and quantitatively determined various oxygen-containing compounds (acids, aldehydes, esters, alcohols, acetals, and ketones) found in the aqueous layer. It was established that among the products of the oxidation of aldehydes and of alcohols (formaldehyde, acetaldehyde, methyl alcohol, and ethyl alcohol, which apparently are derived from the decomposition of the primary products of oxidation), peroxides of the gaseous hydrocarbons predominate. These hydrocarbons must be regarded as products of the cracking of higher hydrocarbons originally contained in the motor fuel.

- 6 -

C-O-N-F-I-D-E-N-T-I-A-L

C-O-N-F-I-D-E-N-T-I-A-L

50X1-HUM

As far as methods for the industrial synthesis of alcohols are concerned, the solution of problems which have a bearing on the direct oxidation of hydrocarbons into alcohols and other oxygen-containing compounds is of the foremost importance, although other methods for the synthesis of alcohols (hydration of unsaturated hydrocarbons, synthesis of ethyl alcohol and other alcohols from carbon monoxide and hydrogen, and oxo-synthesis) must also not be neglected. Oxidation methods are very promising from the standpoint of their application in contemporary organic synthesis based on the conversion of hydrocarbons, because these methods make it possible to obtain directly, without time-consuming intermediate steps, the principal products which are desired. However, difficulties arise in connection with the industrial application of methods of the direct oxidation of hydrocarbons because of the complexity of developing a process which proceeds in the right direction and because of the difficult nature of the separation of multicomponent mixtures of products. In connection with this, a number of theoretical problems pertaining to the kinetics and mechanism of oxidation processes must be solved.

The results of theoretical investigations on the oxidation of hydrocarbons carried out by N. N. Semenov, S. S. Nametkin, A. N. Bashirov, N. M. Emanuel', K. I. Ivanov, and others may be expected to contribute to the solution of the theoretical problems involved. When these problems have been solved, processes for the production of aliphatic alcohols will undoubtedly occupy an important place among newly developed methods of petrochemical synthesis. (12)

#### Kinetics of Oxidation

In connection with the planning of a conference on chemical kinetics and reactivity, which the Department of Chemical Sciences, Academy of Sciences USSR, had scheduled for 1954, N. N. Semenov was charged with the task of compiling a general review of the subject. He did this in the form of a book published in 1954. Members of the Institute of Chemical Physics aided him in compiling the information contained in the book. (14) The data given in the book indicate, among other things, that all chain reactions which are possible from the standpoint of the structural theory, rather than any one reaction at a time, proceed simultaneously in any one system, and that these reactions compete with each other. Depending on their relative velocities, one of the chain reactions will predominate under a given set of conditions. However, there are transitional regions within which the velocities of different chain reactions are so close to each other that a great number of diverse reaction products will be formed.

A chain reaction proceeding over free radicals may also compete with an ordinary (nonchain) monomolecular or bimolecular reaction leading directly to molecular products. However, the activation energy of the second type of reaction is so much greater in comparison with the energy required to activate the first that chain reactions take place preferentially.

As far as the mechanism of the oxidation of hydrocarbons is concerned, the conclusion can be made that at low temperatures hydroperoxides are formed to a predominant extent. When the temperature reaches approximately 250°C, there is primary formation of aldehydes and alcohols, while at still higher temperatures, cracking products are predominantly formed, in addition to aldehydes. The conclusions arrived at on the basis of the theoretical treatment of the chain mechanism of oxidation reactions occurring in this type of conversion are in satisfactory agreement with experimental results.

- 7 -

C-O-N-F-I-D-E-N-T-I-A-L

C-O-N-F-I-D-E-N-T-I-A-L

50X1-HUM

There is an acute need for further developing the theory of chemical processes in order to solve practical problems on which a rapid growth of the chemical industry depends. The aim of theory is to achieve the most efficient control of the rate of chemical conversions and of the direction in which these conversions proceed. Up to the present, the procedures used in chemical technology have been based to a considerable extent on purely empirical data and on the skill of the chemists. In this respect, chemistry compares unfavorably with other branches of science, such as electronics, electrical engineering, the building of aircraft, and atomic energy work, in which a relatively greater amount of theoretical foreknowledge and advance designing is possible.

The majority of modern processes of chemical technology are based on the application of homogeneous or heterogeneous catalysts. The stage reached by theoretical knowledge does not make it possible, as yet, to design the catalysts needed in technology effectively; they are selected empirically. Many processes of organic chemical technology are inadequate, require an excessive number of stages, and are based on the conversion of crude material which is too expensive. Although it is known that reactions can be simplified and cheaper starting material used, this is not being done, because the modified processes cannot be easily controlled. For example, the production of alcohols, aldehydes, and acids by the oxidation of natural gas or petroleum gas is not carried out on an extensive scale as yet for the sole reason that this process cannot be controlled with facility.

The development of such processes would be of immense importance to the chemical industry. They can be developed if a sufficient knowledge of the mechanism of chemical reactions is acquired on the basis of difficult experimental investigations dealing with the behavior of elementary particles (radicals, etc.).(15)

#### Oxidative Cracking

The interrelationships between the processes of cracking, oxidative cracking, and oxidation can best be interpreted in the following manner:

If it is assumed that the reactions involved are of a chain type and proceed over free radicals, the following general scheme which covers all three processes can be postulated:

The radical R, which is formed from the initial molecule, may, in the presence of oxygen, (a) be subjected to scission with the formation of short chains (ordinary cracking); (b) be transformed into the peroxide radical  $ROO\cdot$ , which subsequently undergoes one of the following two transformations: (i) decomposition with the formation of aldehydes and ketones or conversion into a peroxide (oxidation); (ii) stabilization, by rearranging, into an olefin with the formation of  $HC_2$  (oxidative cracking).

In the last process,  $\Delta H \approx 0$ . The type of the conversion is determined by a competition between the processes a, bi, and bii, above. The relative velocities of these processes depend on the structure of the radicals and products of their decomposition. If the interrelationships on which this dependence is based will be completely established, i. e. if it will be possible to tell beforehand which reactions are the most likely for any given radical, it will become possible to predict at which period the radical will begin its transformation into an olefin (and subsequently aromatization), how much oxygen will be needed, and at what temperature the conversion must be carried out. On the basis of similar data, [F. C.] Rice was able to predict the composition of products of ordinary cracking.

- 8 -

C-O-N-F-I-D-E-N-T-I-A-L



C-O-N-F-I-D-E-N-T-I-A-L

50X1-HUM

It will also be possible to predict the principal ways along which the oxidation of light or heavy paraffins will proceed.

One must note that this approach will make it possible to explain and predict changes in the ratio of individual products when the temperature has been changed in cracking or oxidation and changes in the composition of the mixture of oxidation products. It is highly probable that further analysis of chemical data from the standpoint of the concepts that have been developed will contribute to making these concepts useful tools for the advancement of organic chemistry.

With the same purpose in mind, i. e. of establishing the interrelationships between the velocities of elementary reactions of the radical type and the structure of the particles which react, the method that has been outlined must be expanded to cover unsaturated and aromatic hydrocarbons as well as molecules containing various substituents. (17)

As far as the practical application of the principles outlined above is concerned, K. K. Dubrovay has developed an original method for the conversion of crude petroleum materials, i. e. the method of vapor-phase oxidative cracking, based on the introduction of a mixture of the vapor of the crude material and air into the reaction zone. (2)

Very extensive work, both on a laboratory scale and a plant scale, has been carried out in the USSR on oxidative cracking. It has been demonstrated convincingly in this work that petroleum distillates in a mixture with air or oxygen undergo mainly dehydrogenation and scission when subjected to oxidative cracking in the temperature range of 450-600°C. This conclusion is confirmed by the high degree of unsaturation and aromatization exhibited by the liquid products of cracking and also by the relatively low content of carbon dioxide and carbon monoxide in the decomposition gases.

Oxidative cracking is usually carried out by adding a small quantity of air or oxygen to liquid hydrocarbons or hydrocarbons in the vapor state which have been heated to a temperature at which oxygen reacts with them. Air is added continuously at such a rate as to enable chemical interaction of hydrocarbons with the oxygen to maintain the temperature at a sufficiently high level so the reaction can proceed without external heating. The temperature of the cracking is regulated by changing the rate at which air or oxygen is supplied into the reaction zone.

In pyrolysis gases the volume ratio of paraffins to alkenes is always greater than unity and increases with rising temperatures. In gases derived from oxidative cracking, the content of alkenes, by volume, is always higher than that of paraffins or at least equal to it. This makes the gases from oxidative cracking more valuable for purposes of chemical conversion, particularly if blown with oxygen or with an air mixture enriched with oxygen, so that the extent of dilution with inert gases is reduced. The high relative content of alkenes in the gases of oxidative cracking proves that the reactions of synthesis leading to the formation of aromatic hydrocarbons are weakened at this point.

Dehydrogenation under the conditions of oxidative cracking is accompanied by a considerable amount of demethylation. Consequently, the principal product obtained in the vapor-phase oxidative cracking of methylcyclohexane is benzene, while the yield of toluene amounts to only 2.5-3.5%.

Experimental data on the oxidative cracking of n-octane in nitrogen-oxygen mixtures indicate that the effect of the oxygen content on the course of the cracking process is relatively small.

- 9 -

C-O-N-F-I-D-E-N-T-I-A-L

C-O-N-F-I-D-E-N-T-I-A-L

50X1-HUM

The activation energy of the reactions of oxidative cracking of ligroin amounts to 10,400 calories per mol as compared with 48,500 calories per mol in the thermal cracking of the same product. At 700°, the rate of the thermal cracking of ligroin is doubled when the temperature is raised 28°, while the rate of oxidative cracking is doubled when the temperature is raised 75°. The rates of the two types of cracking become equal at 790°. At temperatures lower than 790°, oxidative cracking proceeds at a higher rate than thermal cracking. However, the higher reaction rate in the case of oxidative cracking does not result in any advantages as far as possibilities of reducing the dimensions of the equipment are concerned, because the volume of the products obtained by oxidative cracking with air-blowing exceeds that of the volume of products obtained by ordinary (non-oxidative) vapor-phase cracking. A laboratory comparison of ordinary vapor-phase cracking with air-blowing, oxidative cracking in the presence of oxygen diluted with carbon dioxide or with water vapor, and vapor-phase cracking in a stream of carbon dioxide or water vapor showed that practically the same yields of gasoline, gas, and residue are obtained in all cases when the temperature and all other conditions besides those imposed by the nature of the process are the same. R. S. Yakovlev arrived at the conclusion that feeding air into the cracking zone does not noticeably influence the yield of gasoline. However, the quality of the gasoline and of other products is considerably better when oxidative cracking is used, so that this method is preferred to ordinary cracking. (18)

Oxygen derived from water can be used to produce scission and dehydrogenation of saturated hydrocarbons. L. I. Avramenko and R. V. Kolesnikova investigated the mechanism of the oxidation of ethane with the use of atomic oxygen derived from water vapor that had been subjected to an electrical discharge. The method used by these investigators enabled them to carry out the oxidation without a flame. The products of the reaction of ethane with the gas consisting of O, OH, and H that had been produced by applying an electrical discharge to water vapor were found to be ethylene, formaldehyde, ethyl alcohol, methane, carbon monoxide, and carbon dioxide. The experiments in question led to the conclusion that at temperatures below 100° the radical  $\text{CH}_3\text{-CH=}$  has a greater tendency to rearrange to form ethylene rather than to combine with oxygen to form acetaldehyde. (19)

#### Inhibitors of the Decomposition of Hydrocarbons

To explain the action of substances which have an inhibiting effect on the thermal cracking of hydrocarbons (nitric oxide, propene and higher olefins, etc), some investigators (C. N. Hinshelwood et al) assumed that the reaction proceeds by two mechanisms, a chain mechanism which is easily inhibited by the substance added and a molecular mechanism which is not affected by this substance. According to an investigation carried out by V. A. Poltorak and V. V. Voyevodskiy, data obtained by investigating the products of the cracking of propane with the aid of the deuterium exchange method indicate that a single mechanism is effective in both the inhibited and the uninhibited reaction. If the reaction proceeded mainly by a radical-chain mechanism in the first case and mainly by a rearrangement of bonds in the second, a difference in the degree of deuterium exchange would have been observed, since radicals exchange hydrogen for deuterium faster than molecules. No such difference was found. (20)

The kinetics of the chain mechanism of the decomposition of paraffins in the presence of inhibitors have been subjected to a mathematical treatment by A. D. Stepukhovich. (21) Stepukhovich and members of his group at the Saratov State University imeni N. G. Chernyshevskiy have also carried out an extensive experimental study of the inhibiting effect exerted by olefins and acetylene on the chain decomposition of saturated and unsaturated hydrocarbons. (22, 25)

- 10 -

C-O-N-F-I-D-E-N-T-I-A-L

C-O-N-F-I-D-E-N-T-I-A-L

50X1-HUM

The data on the kinetics of the thermal decomposition of butadiene which have been obtained in this investigation are of particular importance by reason of the significance of butadiene as a crude material for the production of synthetic rubber and also because of the fact that butadiene is formed as an intermediate product in petroleum cracking processes. The data obtained indicate that the decomposition of butadiene is inhibited by acetylene, one of the decomposition products of butadiene. On the other hand, butadiene does not inhibit the thermal decomposition of paraffins (propane, butane, and isobutane).

Butadiene can be produced industrially by the dehydrogenation of butane and butene. (26)

## SOURCES

1. Problemy Okisleniya Uglevodorodov (Problems of the Oxidation of Hydrocarbons), S. R. Sergienko, ed, Academy of Sciences USSR, Moscow, 1954, 223 pp; "Foreword" by S. R. Sergienko
2. Ibid., pp 4-10, "Development of Organic Synthesis Based on the Oxidation of Petroleum Hydrocarbons" by S. R. Sergienko
3. Ibid., pp 13-39, "Development of the Chain Theory of the Oxidation of Hydrocarbons" by N. N. Semenov
4. Ibid., pp 104-108, "Characteristics of the Oxidation of Paraffin Hydrocarbons in the Liquid Phase" by A. N. Bashkirov and Ya. B. Chertkov
5. Ibid., pp 176-174, "Investigations Pertaining to the Oxidation of High-Molecular Hydrocarbons and Petroleum Oils in the Liquid Phase" by N. I. Chernozhukov
6. Ibid., pp 111-123, "The Nature of the Initial Action of Molecular Oxygen on Hydrocarbons of Different Structure in the Liquid Phase" by K. I. Ivanov
7. Ibid., pp 124-139, "Peroxides Which Form in the Autooxidation of Some Alkanes and Cycloalkanes" by K. I. Ivanov, V. K. Savinova, and V. P. Zhakhovskaya
8. Ibid., pp 60-77, "Oxidation of Hydrocarbons in the Presence of Hydrogen Bromide" by Z. K. Mayzus and N. M. Emanuel
9. Ibid., pp 152-166, "Oxidation of Vaseline Oil and Kerosene With the Oxygen of the Air and Nitric Acid" by I. P. Losev and R. N. Smirnov
10. Ibid., pp 177-183, "The Development of Industrial Methods for the Oxidation of Petroleum Hydrocarbons in the Liquid Phase" by V. K. Tsyskovskiy
11. B. A. Krentsel', Osnovy Sintesa Alifaticheskikh Spirtov iz Neftyanykh Uglevodorodov (The Basis of the Synthesis of Aliphatic Alcohols From Petroleum Hydrocarbons), Academy of Sciences USSR, Moscow, 1954, 183 pp, pp 121-149

- 11 -

C-O-N-F-I-D-E-N-T-I-A-L

50X1-HUM

C-O-N-F-I-D-E-N-T-I-A-L

12. B. A. Krentsel', op. cit., pp 172-173
13. A. D. Petrov, *Khimiya Motornykh Topliv* (The Chemistry of Motor Fuels), Academy of Sciences USSR, Moscow, 1953, 511 pp; pp 344-345
14. N. N. Semenov, *O Nekotorykh Problemakh Khimicheskoy Kinetiki i Reaktsionnoy Sposobnosti* (Concerning Some Problems of Chemical Kinetics and Reactivity), Academy of Sciences USSR, Moscow, 1954, 349 pp; pp 3-4
15. Ibid., pp 323-346
16. *Problemy Mekhanizma Organicheskikh Reaktsiy*, Trudy Kievskogo Soveshchaniya 2-5 Iyunya 1952 (Problems of the Mechanism of Organic Reactions, Transactions of the Kiev Conference of 2-5 June 1952), Ye. A. Shilov, ed, Academy of Sciences Ukrainian SSR, Kiev, 1954, 354 pp; pp 40-57, "The Mechanism of Catalysis With Hydrogen Bromide of the Reactions of Hydrocarbon Oxidation" by Z. K. Mayzus and N. M. Emanuel'
17. Ibid., pp 58-77, "The Reactivity of Free Hydrocarbon Radicals" by V. V. Voyevodskiy
18. S. N. Obryadchikov, *Tekhnologiya Nefti* (Petroleum Technology), Part II, 3d ed, Gostoptekhizdat, Moscow-Leningrad, 1952, 408 pp; pp 170-174
19. L. I. Avramenko, R. V. Kolesnikova, "Primary Reactions of Atomic Oxygen With Ethane," Doklady Akademii Nauk SSSR, Vol 89, No 6, Moscow, 1953, pp 1,037-1,046
20. V. A. Poltorak, V. V. Voyevodskiy, "The Single Chain Mechanism of the Thermal Decomposition of Hydrocarbons," Doklady Akademii Nauk SSSR, Vol 89, No 5, Moscow, 1953, pp 889-892
21. A. D. Stepukhovich, "The Kinetics of the Chain Decomposition of Hydrocarbons in the Presence of Inhibitors," Doklady Akademii Nauk SSSR, Vol 89, No 5, Moscow, 1953, pp 889-892
22. A. D. Stepukhovich, A. G. Finkel', "The Kinetics and Mechanism of the Decomposition of Ethane at Low Pressures in the Presence of Propene," Zhurnal Fizicheskoy Khimii, Vol 26, No 10, Moscow, 1952, pp 1,413-1,418
23. A. D. Stepukhovich, A. G. Finkel', "The Kinetics and Mechanism of the Decomposition of Ethane in the Presence of Propene," Zhurnal Fizicheskoy Khimii, Vol 26, No 10, Moscow, 1952, pp 1,419-1,424
24. A. D. Stepukhovich, E. S. Shver, "The Kinetics and Mechanism of the Decomposition of Propane in the Presence of Isobutene and Propene as Inhibitors," Zhurnal Fizicheskoy Khimii, Vol 27, No 7, Moscow, 1953, pp 1,013-1,033
25. A. D. Stepukhovich et al., "The Kinetics and Mechanism of the Decomposition of Hydrocarbons," Zhurnal Fizicheskoy Khimii, Vol 28, No 7, Moscow, 1954, pp 1,174; Vol 28, No 8, pp 1,361-1,370; Vol 28, No 10, pp 1,720-1,724; Vol 28, No 11, pp 1,878-1,881
26. N. I. Smirnov, *Sinteticheskaya Kauchuki* (Synthetic Rubbers), Goskhimizdat, Leningrad, 1954, 456 pp; pp 207-246

- E N D -

- 12 -

C-O-N-F-I-D-E-N-T-I-A-L

50X1-HUM

**Page Denied**